

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-081399

(43)Date of publication of application : 26.03.1996

(51)Int.Cl.

C07C 19/08
C07C 17/389

(21)Application number : 06-214861

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(22)Date of filing : 08.09.1994

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(54) PURIFICATION OF TETRAFLUOROMETHANE

(57)Abstract:

PURPOSE: To obtain tetrafluoromethane of high purity suitable for detergent of semiconductor by bringing tetrafluoromethane containing trifluoromethane as an impurity into contact with a zeolite with a prescribed pore size to reduce the impurities.

CONSTITUTION: Tetrafluoromethane (FC-14) containing trifluoromethane (HFC-23) as an impurity is brought into contact with zeolite or carbonaceous adsorbent of 3.5-11 μ m pore sizes to purify tetrafluoromethane. For example, when a zeolite having 4.2 μ m pore size is used HFC-23 is reduced to less than 10ppm from FC-14 having 12,000ppm HFC-23 content. The adsorption treatment is preferably effected in the liquid phase.

LEGAL STATUS

[Date of request for examination] 15.11.1996

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2924660

[Date of registration] 07.05.1999

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the purification approach of tetrafluoromethane (it abbreviates to FC-14 hereafter). FC-14 are used for the dry etching of a semi-conductor manufacture process, therefore the high grade article is demanded.

[0002]

[Description of the Prior Art] The approach of versatility [manufacturing method / of FC-14 / former] is learned. For example, there is an approach to which a dichlorodifluoromethane is made to react with hydrogen fluoride under existence of a catalyst, an approach to which monochlorotrifluoromethane is made to react with hydrogen fluoride under existence of a catalyst, an approach to which trifluoromethane is made to react with a fluorine, or the approach of pyrolyzing tetrafluoroethylene to FC-14 and carbon. However, the separation is very difficult in order that the trifluoromethane which carries out [trifluoromethane] a byproduction by the reaction or was used as a raw material may form FC-14 and azeotropy mixture which are the specified substance, in manufacturing FC-14 by these approaches. Therefore, by the well-known approach, it is very difficult to manufacture high grade FC-14 which hardly contain trifluoromethane, and development of the advantageous purification approach was desired industrially.

[0003]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the purification approach that high grade FC-14 which hardly contain trifluoromethane can be obtained.

[0004]

[Means for Solving the Problem] This invention relates to the approach of carrying out adsorption treatment only of HFC-23 in FC-14 which contain trifluoromethane (it abbreviates to HFC-23 hereafter) as an impurity selectively by using adsorption actuation in the process in which FC-14 of a high grade are manufactured. In this invention, as an adsorbent, a zeolite is usable, and in order that the zeolite especially whose pore size is 3.5A - 11A may adsorb HFC-23 selectively, it is effective in this object. Moreover, activated carbon and a carbonaceous adsorbent (molecular sieving carbon) of the same kind are also effective.

[0005] According to count, the diameter of a molecule of HFC-23 and FC-14 becomes about 3.7A and about 3.9A, respectively, and is considered that the difference of the diameter of a molecule is small. Therefore, it is presumed that it is difficult to make HFC-23 in FC-14 adsorb selectively only according to the difference of the diameter of a molecule. this invention person etc. examined various the purification approaches including alternative adsorption to this problem. Alternative adsorption needs suitable balance with the polarity of an adsorbent, the dipole moment of an aperture and an adsorbate, and molecule size.

[0006] When in the case of this invention the zeolite as an adsorbent generally tends to adsorb a polar substance and the dipole moment of an adsorbate is considered, HFC-23 have 1.66 debyes and a polarity to FC-14 being zero. In consideration of these, HFC-23 content reduction, such as changing a class,

adsorption treatment conditions, etc. of an adsorbent, was considered wholeheartedly. It is about 12,000 ppm by this result, especially pore size performing adsorption actuation at a room temperature to about 3.5A or more, for example, 4.2A, using the zeolite which has pore size. Depending on reducing the content of FC-14 to HFC-23 containing HFC-23, and getting, and the class of zeolite, the content of HFC-23 is 10 ppm. It became clear that FC-14 of the following were obtained.

[0007] On the other hand, in the zeolite with which pore size has pore size in about 3.5A or less, for example, 3.2A, reduction of a content was hardly accepted. Moreover, when the experiment with the same said of the carbonaceous adsorbent (molecular sieving carbon) which has pore size in about 4A examined, reduction of the content of HFC-23 was accepted. Although any approach of the method of making it contact by the gaseous phase or the method of making it contact by the liquid phase is possible as the approach of adsorption treatment, it is more desirable to make it adsorb by the liquid phase.

Although well-known approaches, such as a batch process and continuous system, can be used for the approach of making it contacting by the liquid phase, two adsorption towers are industrially prepared as the fixed bed, and this will be switched if saturation adsorption is reached. Moreover, since processing temperature and a pressure are also decided depending on those arts, it is not limited especially.

[0008]

[Example] The example of this invention is shown below.

It is 12,000 ppm about HFC-23, filling each up with 10ml (made in union Showa, Inc.) of three kinds of commercial zeolites, and cooling a cylinder after a vacuum drying in the cylinder made from stainless steel with example 1 capacity of 100ml. Each was filled up with FC-14 [40g] to contain, and the gas chromatography analyzed the liquid phase section about 20 hours after, sometimes agitating at a room temperature. A result is shown in a table 1.

[0009]

[A table 1]

ゼオライト No.	液相部のHFC-23濃度 (ppm)
1	trace<10
2	trace<10
3	trace<10

Zeolite No.1. molecular sieves 4A (pore size 3.5A)

2. Molecular Sieves 5A (Pore Size 4.2A)

3. Molecular Sieves 13X (Pore Size 10A)

[0010] By making it contact using the zeolite whose pore size is 3.5-11A by using FC-14 containing HFC-23 as an adsorbent so that clearly from a table 1, the content of HFC-23 is reduced and the content is 10 ppm. It becomes below.

[0011] It is 12,000 ppm about HFC-23, filling each up with 10ml (Takeda Chemical Industries, Ltd. make) of two kinds of commercial carbonaceous adsorbents, and cooling after a vacuum drying like example 2 example 1. Each was filled up with FC-14 [40g] to contain, and the gas chromatography analyzed the liquid phase section about 20 hours after, sometimes agitating at a room temperature. A result is shown in a table 2.

[0012]

[A table 2]

炭素質吸着剤 No.	液相部のHFC-23濃度 (ppm)
1	2580
2	5844

Carbonaceous adsorbent No.1. molecular sieving carbon 4A (average pore size 4A)

2. Molecular Sieving Carbon 5A (Average Pore Size 5A)

[0013] Also when a carbonaceous adsorbent (molecular sieving carbon) is used as an adsorbent so that

clearly from a table 2, the reduction effectiveness of HFC-23 content is accepted.

[0014] It is 12,000 ppm about HFC-23, filling each up with 10ml (made in union Showa, Inc.) of two kinds of commercial zeolites, and cooling after a vacuum drying like the example example 1 of a comparison. Each was filled up with FC-14 [40g] to contain, and the gas chromatography analyzed the liquid phase section about 20 hours after, sometimes agitating at a room temperature. A result is shown in a table 3.

[0015]

[A table 3]

ゼオライト No.	液相部のHFC-23濃度 (ppm)
1	11989
2	10752

Zeolite No.1. molecular sieves 3A (pore size 3A)

2. Molecular Sieves HX-9 (Pore Size 3.2A)

[0016] In the zeolite of less than 3.5A of pore size, content reduction of HFC-23 was not accepted so that clearly from a table 3.

[0017]

[Effect of the Invention] Depending on reducing the content of HFC-23 greatly and getting, and the class of the zeolite, the content of HFC-23 is 10 ppm by making it contact using the zeolite whose average pore size is 3.5-11A by using clearance of HFC-23 in former very difficult FC-14 as an adsorbent according to this invention. It becomes below.

[Translation done.]

JAPANESE

[JP,08-081399,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The purification approach of the tetrafluoromethane characterized by reducing trifluoromethane by contacting the tetrafluoromethane which contains trifluoromethane as an impurity to the adsorbent whose pore size of a zeolite or a carbonaceous adsorbent is 3.5A thru/or 11A.

[Translation done.]